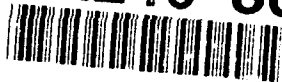


AD-A240 866



**S** **D** **D**  
DUC  
ELECTE  
SEP 20 1991  
**D**

OFFICE OF NAVAL RESEARCH

Contract No. N00014-88-K-0732  
R&T Code b41c011dar

Technical Report No. 40

Synthesis, Characterization, and Electropolymerization  
of Ferrocene Substituted Anilines

by

Colin P. Horwitz, Norman Suhu, and Gregory C. Dailey

Prepared for Publication

in

Journal of Electroanalytical and Interfacial Electrochemistry

Rensselaer Polytechnic Institute  
Department of Chemistry  
Troy, NY 12180

May 1991

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimite

91-11084



91 11084

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 40			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Department of Materials Science and Engineering		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) University of Pennsylvania 3231 Walnut Street Philadelphia, PA 19104-6272			7b. ADDRESS (City, State, and ZIP Code) Dr. Robert Nowak, Chemistry Division ONR, 800 North Quincy Street Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division, ONR 800 North Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
					WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Synthesis, Characterization, and Electropolymerization of Ferrocene Substituted Anilines					
12. PERSONAL AUTHOR(S) Colin P. Horwitz, Norman Suhu, and Gregory C. Dailey					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 5/89 TO 5/91		14. DATE OF REPORT (Year, Month, Day) 1991, June 12	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Submitted to: Journal of Electroanalytical and Interfacial Electrochemistry					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Aniline, ferrocene,		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The synthesis and electrochemical properties of aniline and aniline like molecules substituted with ferrocene are described [(C<sub>5</sub>H<sub>5</sub>)Fe (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>NHR) where R= C<sub>6</sub>H<sub>5</sub>, 1, C<sub>6</sub>H<sub>5</sub>-3-NH<sub>2</sub>, 2, C<sub>6</sub>H<sub>5</sub>-3-OH, 3, and (CH<sub>2</sub>)<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub>, 4]. All compounds polymerize upon electrochemical oxidation of the aromatic amine portion of the complex in a CH<sub>3</sub>CN solution containing Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. The phenol substituted complex shows its best polymerization characteristics when approximately one equivalent of NEt<sub>3</sub> is added to the electrolysis solution. The polymers, characterized by cyclic voltammetry, show well defined couples for the ferrocene but there is no electrochemical indication that the polymer backbones are electroactive. Spectroelectrochemical measurements show changes in the visible absorption spectrum characteristic for formation of the ferricinium cation, λ<sub>max</sub> = 620 nm, in all of the polymers upon oxidation. In the case of the polymer from 2, an intense absorption at 480 nm also is recorded which suggests that the polymer backbone is in fact electrochemically active.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Gregory C. Farrington			22b. TELEPHONE (Include Area Code) 215 898 6642		22c. OFFICE SYMBOL

# SYNTHESIS, CHARACTERIZATION, AND ELECTROPOLYMERIZATION OF FERROCENE SUBSTITUTED ANILINES

Colin P. Horwitz, Norman Suhu, and Gregory C. Dailey  
Department of Chemistry, Rensselaer Polytechnic Institute, Troy NY, 12180-3590.

## ABSTRACT

The synthesis and electrochemical properties of aniline and aniline like molecules substituted with ferrocene are described.  $[(C_5H_5)Fe(C_5H_4CH_2NHR)]$  where  $R = C_6H_5$ , **1**,  $C_6H_5-3-NH_2$ , **2**,  $C_6H_5-3-OH$ , **3**, and  $(CH_2)_2NHC_6H_5$ , **4**. All compounds polymerize upon electrochemical oxidation of the aromatic amine portion of the complex in a  $CH_3CN$  solution containing  $Bu_4NClO_4$  as supporting electrolyte. The phenol substituted complex shows its best polymerization characteristics when approximately one equivalent of  $NEt_3$  is added to the electrolysis solution. The polymers, characterized by cyclic voltammetry, show well defined couples for the ferrocene but there is no electrochemical indication that the polymer backbones are electroactive. Spectroelectrochemical measurements show changes in the visible absorption spectrum characteristic for formation of the ferricinium cation,  $\lambda_{max} = 620\text{ nm}$ , in all of the polymers upon oxidation. In the case of the polymer from **2**, an intense absorption at 480 nm also is recorded which suggests that the polymer backbone is in fact electrochemically active.

The ferrocene polymers that have been described exhibit a number of desirable properties which may lead to their use in practical devices. These polymers are quite stable to standard electrochemical conditions, show good stability to storage at ambient conditions, and the monomers can be synthesized using simple techniques. Furthermore, the mild positive potentials used in forming the films simplifies device fabrication. All of these aspects offer considerable improvements over existing methodologies for preparing electropolymerized polyferrocene films.

The methodology of incorporating a redox active transition metal complex onto a possible electronically conducting organic backbone holds promise for preparing novel materials. As demonstrated for the polyphenylene oxide like polymers, a synergistic effect can occur between the different components. In this example, the ferrocene aids in propagating charge through what normally would be an insulating film while the phenol backbone provides a useful means for immobilizing the ferrocene. Studies are ongoing to determine the generality of the present approach to polymer film formation.

Accession For	
NTIS	CRAND
DTIC	TAB
Unannounced	
Justification	
By	
Distribution	
Availability	
Dist	Overseas Special
A-1	



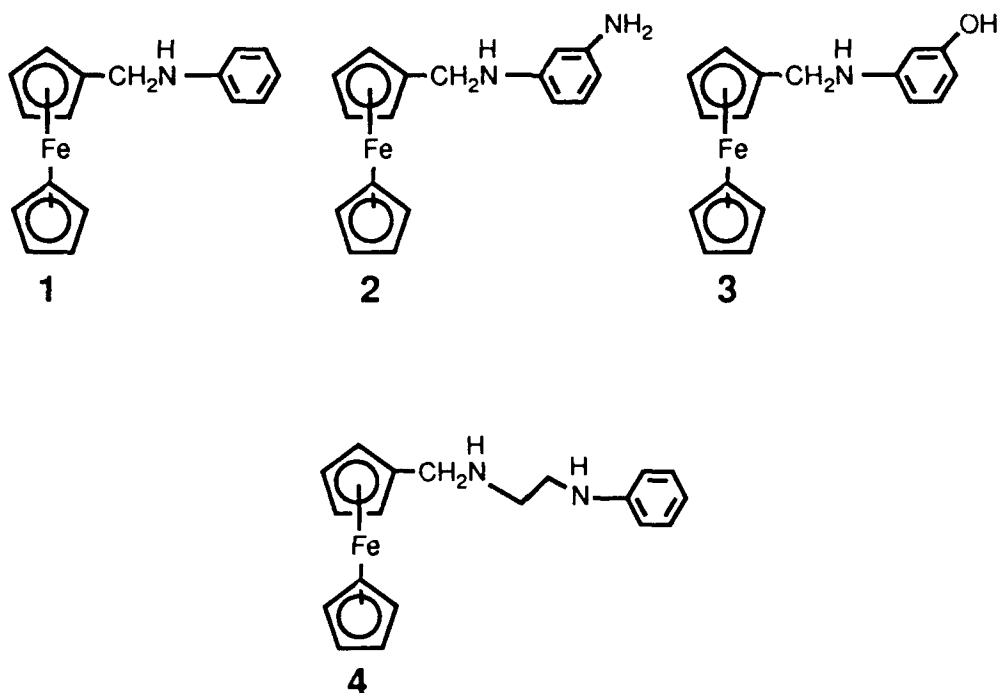
## RESULTS

- All compounds can be electropolymerized
- Compound 2 is the best method to form polyphenylene oxide films - a new electronic conductor
- Compound 3 may have an electronically conducting polyaniline backbone
- Compound 4 has poor film forming properties
  - a) Decrease free volume for ion motion
  - b) Alkyl chain is hydrophobic and rejects ions
- Promise of new materials with unique properties is being realized

## COMPOSITE ELECTRONIC - REDOX HOPPING CONDUCTORS

- Organic polymers which are electronically conducting may be used for battery electrodes
- Redox hopping conductors prepared from metal complexes allow control of ion concentration
- Composite materials should have unique and novel properties

## Materials synthesized, characterized, and electropolymerized



- 1) Polyaniline or polyphenyleneoxide like backbones
- 2) Metal ion can be oxidized to control anion levels
- 3) Compound 4 may be viewed as a polyethyleneimine analog